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<p>(21) International Application Number: PCT/IB98/01395</p> <p>(22) International Filing Date: 9 September 1998 (09.09.98)</p> <p>(71) Applicant (for all designated States except US): FULLTECHNOLOGY, LTD. [CY/CY]; Vision Hire Building, Office No. 201, 3rd floor, Corner M. Kontopouli & Kalomiri, 3030 Limassol (CY).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): GAMZINE, Mikhail [RU/CY]; 11A Kanika Olive Gardens, Amfictionous Street Germasoya, 4046 Limassol (CY). NOVIKOV, Andronit [RU/CY]; Villa 20, 7 Natara Street, Mesa Geitonia, 4007 Limassol (CY). GALEEV, Valeri [RU/CY]; Villa 20, 7 Natara Street, Mesa Geitonia, 4007 Limassol (CY).</p> <p>(74) Common Representative: FULLTECHNOLOGY, LTD.; Vision Hire Building, Office No. 201, 3rd floor, Corner M. Kontopouli & Kalomiri, 3030 Limassol (CY).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report.</p>
<p>(54) Title: METHOD AND DEVICE FOR PRODUCING MICROCLUSTERS FROM ATOMS OF DIFFERENT ELEMENTS</p> <p>(57) Abstract</p> <p>The invention regards to the chemical technologies particularly to the field of producing microclusters, that are the finest groups of atoms, the number of which varies from two to several hundreds, and possess unique characteristics. The main task of the proposed method and device is to develop a technology that provides the possibility to manufacture a large range of microclusters with set compositions under industrial conditions with comparatively low power inputs and greater outputs of the end product. To attain that our method, which is based on the vaporization of carbon-containing material by means of an electrical arc, maintained by the connection of the electrodes to the power source, resulting in the extraction of microclusters from the produce of the thermal decomposition, in comparison to the prototype, suggests using, as an additional carbon-containing material, the dielectric solution of at least one of the elements of microcluster in a liquid hydrocarbon, and, simultaneously, the electrodes, one of which is a graphite, whereas the others, made of a material containing the element of the microcluster.</p>		

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Method and Device for Producing Microclusters from Atoms of Different Elements.

DESCRIPTION

The invention is related to chemical technologies particularly to the field of producing microclusters. Microclusters, as being the finest groups of atoms, the number of which varies from two to several hundreds, may find its effective use in Chemistry, Physics, medicine and other areas of scientific research. For the first time microclusters were obtained from carbon and named Fullerenes. Fullerenes are comparatively well studied and the methods of their industrial production are known and used.

The process of producing fullerenes from atoms of different elements is less developed, that is why for the invention of our technology we used all the experience available regarding the production of fullerenes, both simple (C_{60}) and complex (C_{70} , C_{76} , C_{84} , etc.).

The existing method and device for obtaining fullerenes (application for the invention PCT № 92.04279 "New form of carbon" with the priority MIK CO 1 B 31/00, published on 19.03.92) suggests that graphite elements are placed in a contained volume to which inert gas is added. In the given conditions and by means of a vaporizer, the graphite evaporates. Inert gas is being used not only as a low active chemical milieu, but a cooling agent as well. The obtained fullerenes are the vapors of carbon.

The disadvantage of this method and device for obtaining fullerenes by evaporation of a solid substance is that this process is power consuming and demands very high power inputs. As a result the cost of fullerenes amounts to several thousands of dollars per gram.

In the existing technology of producing microclusters (presented by Michael A. Duncan and Denis H. Rouvrey in their work called "Microclusters" ("In the world of Science", Russian edition, № 2, 1990)) the impulsive laser is used. First the metal is evaporated by the laser and then the resulting vapors of the metal are run through a cylindrical canal containing helium current, and, upon coming out from the canal, condensation takes place forming clusters of different sizes. The mixture of gas and clusters is released into a vacuum chamber, where it expands rapidly, cooling down almost to absolute nil, after which the clusters are ionized by means of ultra-violet laser radiation and accelerated in an electric field for a set distance, after which they are sorted out by weight into "sets".

The above stated method allows the production of clusters practically from any matter, which can take a solid state. The so obtained clusters consist of a mixture of different materials. However, the industrial use of this technology is limited due to the complicated tackle. The process of obtaining clusters by means of this technology is quite power consuming and as a result of that the cost of the final product is high.

The method and device chosen by us as prototype (N.Belov, A.Tokarevskih, N.Nadejdin, U.Odintsova, I.Sukhov. "The influence of working atmosphere pressure and composition on the syntheses of fullerenes". In the magazine "Physics and chemistry of Materials Treating" № 3 1997, pages 115-117) is the closest in its technical nature to our proposed technical solutions.

The above mentioned method is based on the fact that in the medium of inert gas, argon, the graphite electrodes are influenced on by the electric arc (current of 115 A, voltage of 25V) under the changing pressure of the medium.

This installation consists of a cylindrical chamber with water cooling off its walls, in which two electrodes are placed horizontally opposite each other and connected to the current supplying system. One electrode is a pivot (anode) and the other a washer-shaped (cathode). The upper part of the chamber has openings giving access to a double-walled vessel. The gap between the vessel's walls is filled with nitrogen (which acts as a nitrogen trap for the forming volatile substances). During combustion of the electrical arc the process of graphite vaporization and forming of fullerenes takes place.

Although the utilization of the nitrogen trap allows the increase in more than double the output of fullerenes, obtaining fullerenes in such a setting and by this method is comparatively ineffective due to the high power inputs. This shortcoming resides in the fact that on the basis of this method lies a power-consuming process of graphite vaporization.

The aim of our method and device is to develop a technology and equipment which could provide the industrial production of microclusters with a set composition and with a comparatively low power consumption plus a higher output of the end product.

To solve the above mentioned task, our method is based on the vaporization of carbon-containing material by means of an electrical arc, maintained by the connection of electrodes to the power source, resulting in the extraction of microclusters from the produce of the thermal decomposition.

In comparison to the prototype, we are using, as an additional carbon-containing material, the dielectric solution of at least one of the elements of microcluster in a liquid hydrocarbon, and simultaneously the electrodes, one of which is a graphite, and the others made of a material, containing the element of the microcluster.

The proposing method allows the production of microclusters from practically any material. In view of this, two kinds of materials have to be applied. Conductors, to make the electrodes, and dielectrics dissolved in liquid hydrocarbon. By purposely changing the material of electrodes and the composition of the dielectric solution, one can produce a microcluster with a different set composition.

For the making of electrodes any electroconductive material can be used, provided it contains atoms necessary to be found in the microcluster. On the other hand, the dielectric solution has to contain an element, or group of elements, essential to be in the microcluster.

By way of illustration, an electrode of any of the following materials could be used : Iron, Nickel, Chrome, Aluminum, Copper, Tungsten, Molybdenum, Gold, Silver, Vanadium, Tin, Tantalum, Scandium, Iridium, Titanium, Graphite and so on. Regarding the dielectric solution, a variety of liquid hydrocarbons could be utilized, such as industrial oils, transformer oil, spindle oil, any lubrication oils as such, or their mixtures, provided Silicon, Germanium, Gallium, in other words, any of dielectric category, are dissolved within these oils. Moreover, it is important to point out that these oils could be either clean or already "used".

This method is quite simple and therefore may find its use extensively in the industry. Its application will allow considerable economy in the consumption of the electric power, and simultaneously a notable increase in the output of the end product.

Since our method presupposes the extraction of carbon not only from the electrodes, as is offered in the prototype, but from the solution as well, the result of which is lower power inputs. Furthermore, this method allows the use of inexpensive (used oils) basic products for the production of microclusters, the outcome of which is a reduced prime cost of the final product.

To secure an even higher increase of the output, it is necessary to carry out the process of vaporization in a hermetically sealed chamber without the access of air. To insure the safety of the process, the excess pressure, which is constantly increasing due to the release of gases during the vaporization of hydrocarbons, should be kept at the level of $0.2 - 1 \text{ kg/cm}^2$.

To carry out this method, a setup, similar to the prototype, consists of a body, in which electrodes of opposite polarities are placed and connected to a power source. In contrast to the prototype, in the body's cavity a plate made of insulating material is installed, separating it into two volumes, which are connected by throughout openings in the plate, and stationary electrodes are fastened to the plate from below, partially overlapping the openings at the same time. In the cavity of the openings, mobile electrodes are installed in such a way that they could move within the openings.

The construction of this device is so designed that the method could be applied in laboratories as well as on an industrial scale. By employing at least two stationary and one mobile electrodes the device allows the realization of a short-lived, self-regulating, periodically repeated process of vaporization of the basic material needed in the microcluster, and at the same time it does not require the expenses for specific equipment. The stationary electrodes are connected to opposite poles of the power source, the mobile electrode encloses them, and gases generated during vaporization of the material by electric discharge force the mobile electrode upwards, opening the circuit, after which the mobile electrode collapses under its own weight, discharging the circuit again, causing the process to repeat itself.

To obtain a hermetic mode of operation the body requires a hermetic hatch. The excess pressure, which is formed by gases generated during the decomposition of the liquid hydrocarbon,

is kept at the necessary level by means of a pressure regulating device, such as a pressure gauge installed to the body and a pressure valve controlling the outflow of the generated gases.

By having mobile graphite electrode manufactured in a spherical-shape, a pointed contact with the stationary electrodes is achieved, resulting in an increase of the power density, simultaneously reducing the probability of "adhesion" of the spherical electrode to the stationary electrodes.

Following explains the invention on a given sample.

In figure 1 the device for producing microclusters from atoms of different elements, is schematically presented in cross-section.

In figure 2, the construction of the appliance with opened hatch is schematically presented.

The device, shown in fig.1, consists of a metal body (1), where two bearing metal shelves (2) are fastened. An insulating plate (3) is placed horizontally on the shelves and has six throughout vertical openings of 14mm in diameter (4). Electrodes of opposite polarities (5 / 6) are attached to the insulating plate from below, in such a way that they overlap the openings by 4mm, preventing mobile electrodes (7) from slipping through. The diameter of the mobile electrodes has to be less than that of the openings to provide its free movement.

For the realization of this experiment, graphite electrodes (5/6) were used. Even though, in practice other materials were applied too, such as Iron, Nickel, Chrome, Aluminum, Copper, Tungsten, Molybdenum, Gold, Silver and others.

The required dielectric solution is poured into the main body (1) above the level of the insulating plate (3). In our case, the solution of silicon-organic rubber has been used. However, the application of "used" industrial, transformer and spindle oils or any of their mixtures has shown good practical results.

For safety insurance of the process, the body (1) is hermetically sealed by a hatch (8), to which a pressure gauge (9) and a valve (10), allowing the gas, released during the decomposition of hydrocarbons, to be expelled and for keeping the excess pressure within the limits of 0.2 - 1 kg/cm², are installed.

The process of producing microclusters is conducted as described below.

By means of leads (not shown on the fig.) the electrodes (5/6) are connected to the electric power source of 25-70 V, causing the mobile electrodes (7) to short circuit with the electrodes (5/6) provoking electric arcs, which cause a heating up of the solution. As a result, a decomposition of the solution takes place with the isolation of gaseous products and microclusters of silicon and carbon. The forming gaseous products are forcing the mobile electrodes (7) over the electrodes (5/6), leading to the opening of the electric circuit. Next the gaseous products release

through the openings (4), causing the mobile electrodes (7) collapse, locking the electrodes (5/6) again and the process recurs. Isolated gases fill the space between the solution and the hatch.

With the aid of a pressure gauge (9) the amount of pressure is controlled. As soon as the pressure reaches the maximum limit the valve (10) opens and developed gases are partly let out until the required pressure is resumed. With this procedure the excess pressure is kept within the limits of 0.2 - 1 kg/cm².

The synthesized microclusters are contained in a solution in a state of suspension. Their separation is conducted by centrifugal force and extraction.

Hence this device and method allows the production of different combinations of complex microclusters, which could be attained by the following:

1. Changing of materials of stationary electrodes (Iron, Nickel, Chrome, Aluminum, Copper, Tungsten, Molybdenum, Graphite, Gold, Silver, Vanadium, Tin, Tantalum, Scandium, Iridium, Titanium, etc...).
2. Selecting of the dielectric solution required for microcluster (in our case, a solution of silicon-organic rubber).

The presented technology and device allows the production of a comparatively wide class of microclusters. Furthermore, we have a considerable increase in output of the end product and low power inputs. That makes it possible to be used on an industrial scale.

Note: the daily capacity of the device is 400 liters with power consumption of 96 kW/h.

CLAIMS.

1. The method of producing microclusters from atoms of different elements, one of which is carbon, based on the vaporisation of carbon-containing material gained by the influence of the electric arc, which is reached by the connection of electrodes to a power source, with a subsequent separation of microclusters from the products of thermal decomposition, differs, because as an additional carbon-containing material, a dielectric solution of at least one of the elements of the microcluster in liquid hydrocarbon, is used, and the electrodes are made of a material which contains an element that is a component of the microcluster composition, and in addition to that, one of them being a graphite electrode.

2. The method stated in paragraph 1 differs, because the process of the vaporisation is carried out with the pressure level being at 0.2 - 1 kg/cm² in a hermetically sealed chamber.

3. The method stated above in paragraph 1 differs, because, as elements of the dielectric solution, the semi-conductors can be applied (such as, silicon, germanium) if they are dissolved in liquid hydrocarbon, which could be industrial oil, transformer or spindle oils and any of their mixtures, pointing out that these oils could be either clean or already "used".

4. The Method stated above in paragraph 1 differs, the reason being, that electrodes can be made of electroconductive materials such as Iron, Nickel, Chrome, Aluminum, Copper, Tungsten, Molybdenum, Gold, Silver, Vanadium, Tin, Tantalum, Scandium, Iridium, Titanium, Graphite and so on.

5. The device for producing microclusters, which consists of a body, in which electrodes of opposite polarities are installed and connected to a power source, differs, by that, that the body is hermetically sealed, and in its cavity, which is partly filled with a dielectric solution, a plate made of insulating material is placed, separating it into two volumes, which are connected by the throughout openings made in the plate, and the stationary electrodes are fastened to the plate from below, partially overlapping the openings at the same time, when the mobile electrodes are placed into the cavity of each opening, in such a way that they could move within the openings.

6. The device described above in paragraph 5 differs, because the stationary electrodes are made of a material which contains an element of the microcluster.

7. The device described in paragraph 5 differs, by that, that the mobile electrode is made of spherically-shaped graphite.

8. The device described in paragraph 5 differs, reason being, that it is additionally equipped with a hatch, to which a regulating pressure device is installed, that hermetically seals the body.

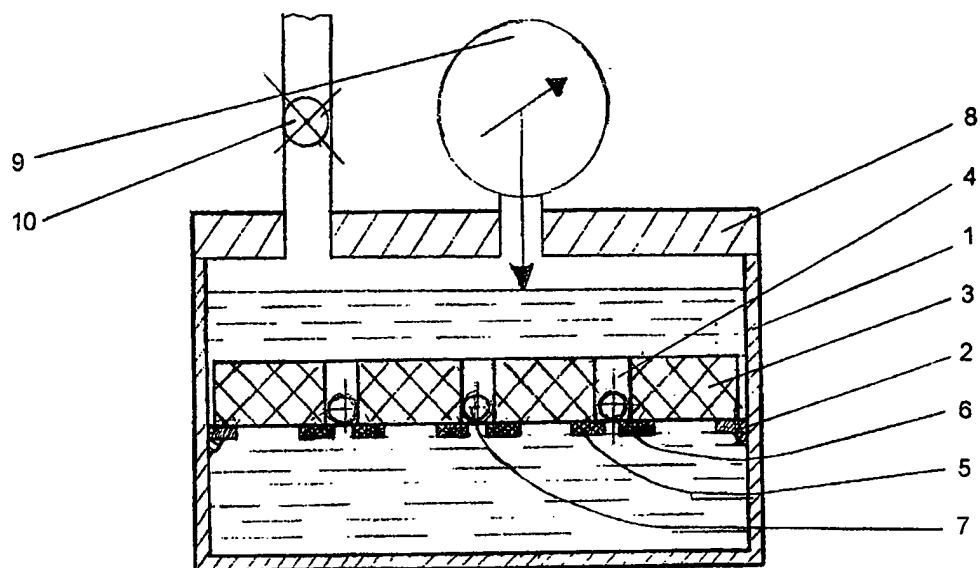


Figure 1.

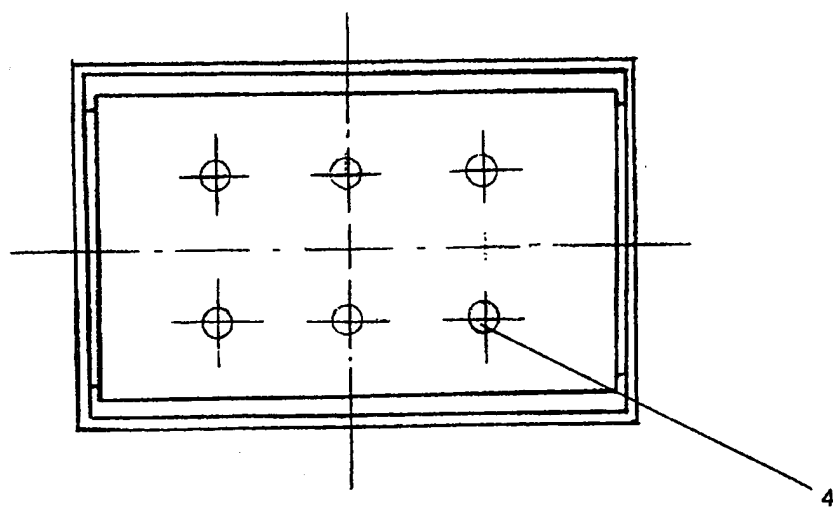


Figure 2.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB 98/01395

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C01B31/02

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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 93 22239 A (UNIV RICE WILLIAM M) 11 November 1993 see page 9, line 17 - page 35, line 11 ---	1
A	US 5 593 742 A (LUX ROBERT A ET AL) 14 January 1997 see column 1, line 56 - column 2, line 39 ---	1
A	US 5 466 430 A (CASTLEMAN JR ALBERT W ET AL) 14 November 1995 see column 5, line 15 - line 49 ---	1
A	DE 40 24 515 A (PHILBERTH KARL ;PHILBERTH BERNHARD (DE)) 20 February 1992 see column 5, line 23 - line 36 -----	1

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INTERNATIONAL SEARCH REPORT

Information on patent family members

I. International Application No

PCT/IB 98/01395

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9322239 A	11-11-1993	NONE	
US 5593742 A	14-01-1997	NONE	
US 5466430 A	14-11-1995	NONE	
DE 4024515 A	20-02-1992	JP 6324167 A	25-11-1994

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